

TIME-RESOLVED RAMAN SPECTROSCOPY OF SINGLE PARTICLE CARBON ELECTRODES

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INTRODUCTION

Recent implementation of Raman microscopic techniques in our laboratory made it possible to record *in situ* Raman spectra of single μm -size particles of LiMn_2O_4 particles embedded in a Au foil substrate as a function of the applied potential.¹ This work extends the scope of such preliminary studies to the acquisition of time-resolved Raman spectra of carbon particles embedded in Ni foils in electrolytes of relevance to Li-ion batteries following application of a potential step. Analysis of these data enabled the state of charge of single particles within the volume probed by the laser beam to be determined in real time.

EXPERIMENTAL

Particles of KS-44 graphite were embedded in thermally annealed Ni foils using procedures described elsewhere.² Except for very minor modifications, the spectroelectro-chemical cell used for these studies was the same as that employed in earlier *in situ* Raman studies.² Raman spectra were obtained with a Raman 2000 system (Chromex Inc., Albuquerque, NM) incorporating a microscope attachment. A Super-Notch-Plus filter (Kaiser Optical Systems, Inc., Ann Arbor, MI) was used to remove the primary beam. All of the data were obtained with the slit width set at $50\text{ }\mu\text{m}$ at a spectral resolution of 2 cm^{-1} . A forced air-cooled CCD system with 1024×256 pixels (Photometrics, Roper Scientific, Tucson, AZ) was used as the photon detector. A 532 nm beam of a Verdi laser (Coherent) focused through a 20X Olympus microscope onto a region of the embedded particle electrode of ca. $5\text{ }\mu\text{m}$ in diameter was used as the excitation source at powers of about 8 mW. The beam impinged on the surface at an incident angle of ca. 90° and the scattered light was collected by the microscope in the 180° backscattering geometry. During potential step experiments, the acquisition time for each spectrum was 5 s. At all other times, the beam was blocked to reduce possible effects induced by local heating and/or photodecomposition (see below). All measurements were performed in 1M LiClO_4 in EC/DEC (1:1 v/v) at room temperature using the same chemicals specified elsewhere.² Potential control was achieved using a Pine potentiostat and the electrochemical data collected in a PC via a digital current to voltage converter.

RESULTS AND DISCUSSION

Fig. 1 shows a typical cyclic voltammetry curve of KS-44 graphite particles embedded into a Ni substrate in 1M LiClO_4 in EC/DEC (1:1 v/v) solution recorded at a scan rate of 0.1mV/s displaying characteristic features associated with formation of Li intercalation compounds.^{3,4} A series of Raman spectra for single particles (not shown here) were recorded during these very slow scans, yielding results in agreement with those reported using more conventional electrodes.^{5,6}

Fig. 2 shows a series Raman spectra acquired continuously for a single KS-44 graphite particle $8\text{ }\mu\text{m}$ in diameter following a potential step from 0.7 V to 0.05 V.

Each of these spectra were fitted with single or multiple Lorentzians functions and compared with spectra collected during the voltammetric cycles. In this fashion direct correlations could be established between the Raman spectral features and the state of charge of the volume of the particle probed by the laser beam as a function of time. The results of such an analysis are given in Fig. 3, which shows a plot of the potential (or state of charge) as measured spectroscopically and the time elapsed following application of the potential step for particles of 8 and $25\text{ }\mu\text{m}$ in diameter. Based on reported values of the diffusion coefficient of Li in the graphite lattice^{7,8} and the actual size of the particles, the times required to achieve equilibration appear quite reasonable. The results of these experiments open new prospects for acquiring *in situ* time-, and space-resolved images of the state of charge of materials within operating electrodes in battery-type environments, which could then be compared directly to information derived from theoretical calculations.

ACKNOWLEDGEMENTS

Support for this work was provided by DOE-BES and a grant from NEDO, JAPAN.

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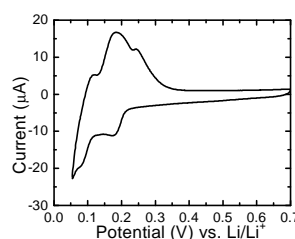


Fig. 1. Cyclic voltammogram of KS-44 graphite particles embedded into a Ni foil in 1M LiClO_4 in EC/DEC (1:1 v/v) solution. Scan Rate: 0.1 mV/s.

Fig. 2. Series Raman spectra recorded continuously for a single KS-44 graphite particle $8\text{ }\mu\text{m}$ in diameter following a potential step from 0.7 V to 0.05 V.

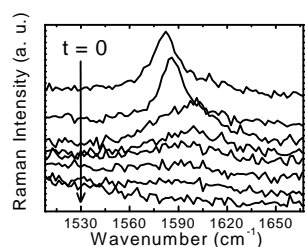
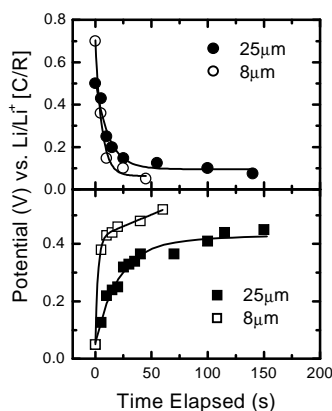


Fig. 3. Plots of the state of charge measured spectroscopically vs time elapsed following a potential step from 0.05 to 0.7 V (Upper Panel) and from 0.7 to 0.05 V (Lower Panel) for KS-44 particles of $8\text{ }\mu\text{m}$ (open symbols) and a potential step from 0.05 to 0.5V (Upper Panel) and 0.5 to 0.05 V (Lower Panel) for particle of $25\text{ }\mu\text{m}$ in diameter (solid symbols).